Novel symmetry in the growth of Gallium Nitride on Magnesium Aluminate substrates

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ABSTRACT

The growth of GaN by metalorganic-chemical vapor deposition on (111) and (100) magnesium aluminate ($MgAl_2O_4$) substrates is examined using transmission electron microscopy. The results indicate that mainly wurtzite GaN is grown for both orientations. On the (11 1) substrate the following epitaxial relationship is observed: (0001)GaN II (11 1) $MgAl_2O_4$ and [11$\bar{2}$0]GaN II [1 $\bar{1}$0]$MgAl_2O_4$. During the early stages of the (100) growth, four orientations of the wurtzite phase and a zinc-blende phase, are formed. With increasing thickness, one of the wurtzite orientations dominates, with the epitaxial relationship being (1$\bar{1}$01)GaN II (100)$MgAl_2O_4$ and the [1 120](.iaN near] y parallel to [011]$MgAl_2O_4$. This choice of growth orientation appears to be determined primarily by the nature of the interfacial bonding, with the basal plane of each of the four wurtzite GaN variants being nearly aligned along one of the four { 111) planes intersecting the (100) surface of the $MgAl_2O_4$.

Epitaxial GaN films have recently attracted much interest due to their optoelectronic applications in the blue/ultra violet regime and for their high temperature stability. [1]GaN can exist in two crystalline structures: wurtzite and zinc-blende, with the wurtzite phase being more commonly grown epitaxially. The zinc-blende phase, however, is expected to have lower activation energies for dopants[2] than the wurtzite GaN and also to be crystallographically amenable for the fabrication of cleavage facet mirrors necessary for laser diodes. Since bulk GaN substrates are not currently available, the films are generally grown on basal plane sapphire substrates. Sapphire is the substrate of choice because of the case of surface cleaning and its stability at the high temperatures required for GaN growth. The lattice mismatch (Ad/et) of GaN is about 14% for growth on basal plane sapphire. This high lattice mismatch results in an extremely high density of structural defects in the GaN layer. Therefore, the search for a substrate having a closer lattice match to GaN is being actively pursued.

GaN has been grown on silicon terminated 6H-SiC substrates which have the closest lattice match to GaN (Δd/d = 4%). However, these surfaces are extremely hard to clean. Zinc-blende GaN has been grown on (100) oriented GaAs and Si substrates.[3,4] Again, high lattice mismatch (20%) poses a significant problem with GaN growth on these substrates and in the case of GaAs the problem of substrate decomposition exists at the high growth temperatures required for GaN growth.

in the present study, the growth of GaN by low pressure metalorganic chemical vapor deposition (LPMOCVD) on cubic $MgAl_2O_4$ substrates was examined. Cubic $MgAl_2O_4$ has a spincl-type crystal structure with the oxygen atoms forming a face-centered-cubic sublattice and the Al and Mg atoms occupying the octahedral and tetrahedral sites, respectively. These substrates have a lower lattice mismatch (Ad/d = 10%) with GaN than sapphire, arc easy to clean and arc stable at high growth temperatures.

GaN films were grown on nominally (111) and (100) oriented $MgAl_2O_4$ substrates in an LPMOCVD system at 76 torr. These orientations were chosen so that the (111) substrate having three-fold symmetry would promote wurtzite GaN growth and on the four-fold symmetric (100) substrate the zinc-blende phase would be grown. The source gases used were triethylgallium and ammonia. The films were grown using a two-step process. A thin (~200Å) 'buffer' layer was grown at about 550°C, followed by growth at about 1000°C for the remainder of the film (few microns). TEM specimens were prepared using standard procedures of mechanical thinning followed by argon-ion milling at 5kV and 0.5mA to achieve electron transparency. Subsequently, the GaN films were characterized by transmission electron microscopy (TEM) using a Topcon 002B and a JEOL 4000FX high resolution microscopes operating at 200 and 400kV respectively. The (1 11) oriented substrates were also examined using a JEOL Atomic Resolution Microscope at the National Center for Electron Microscopy, Berkeley, CA.

As expected, the GaN film grown on (11 1) $MgAl_2O_4$ was wurtzite single crystal and had the following orientation relationship with the substrate: (0001)GaN II (111)$MgAl_2O_4$ and [1120]GaN II [1 $\bar{1}$0]$MgAl_2O_4$. The GaN film contiguous to the interfacial region exhibits a high density of stacking faults (Fig.1). However, the crystal linity of the GaN film is comparable to that of good quality GaN films grown on sapphire substrates. A (110) faceted $MgAl_2O_4$ step (see arrow) is seen at the interface, The step does not appear to introduce any additional defects in the GaN layer.

On the (100) $MgAl_2O_4$ substrate, a far more complicated microstructure was observed at the heterointerface. Instead of a single zinc-blende phase as would be expected from the symmetry constraints, the GaN film was found to contain five different regions, four being wurtzite orientation variants and one zinc-blende phase. Basal plane (0002) lattice fringes were clearly observed from two wurtzite variants which have mirror symmetry across the substrate (0$\bar{1}$1) plane, and having their <1 1 $\bar{2}$0> axes parallel to the [0 1 1] axis of the substrate. Figure 2 shows the presence of three domains, two wurtzite

variants and a zinc-blende phase. The wurtzite domains appear to have a high density of stacking faults whereas the zinc-blende GaN domains, albeit small in size, are relatively defect free. For the other two wurtzite variants. the so-called 'rotated wurtzite' (Fig. 2) only the ($1\bar{1}01$) planes were clearly resolved since in these cases the direction orthogonal to the [$11\bar{2}0$] axis namely the [$1\bar{1}0\bar{2}$] axis, is nearly parallel to the [011] axis of the substrate.

With increasing layer thickness, site-competition appears to have occurred during the growth, with the wurtzite becoming the dominant phase in the upper layers of the film as evidenced by a large area diffraction pattern from the film and substrate (Fig. 3). Note that the $(0001)_{GaN}$ spot is not aligned with the $(1\bar{1}1)_{MgAl_2O_4}$ spot on the diffraction pattern. in fact, there is a small angle (- 4°) between the two. Similarly there is a (-2°) tilt between the $(1\bar{1}01)_{GaN}$ plane and the $(200)_{MgAl_2O_4}$ plane. '1'here appears to be little distortion in the angle between the $(000\,2)_{GaN}$ and the $(1\bar{1}01)_{GaN}$ planes; the measured value is close to the relaxed value of -62°. Thus the overall orientation relationship for the wurtzite film can be expressed as the following: $(1101)_{GaN}$ marl y parallel to $(100)_{MgAl_2O_4}$ and the $[11\bar{2}0]_{GaN}$ parallel to $[01\,1]_{MgAl_2O_4}$. temperature, geometry, facetting, bonding.

The experimental results point to substrate surface symmetry being a factor in the choice of epitaxial orientation for the GaN film. For growth on $(111)_{MgAl_2O_4}$ the orientation relationship is as intuitively expected from the match of the three fold symmetries of the substrate surface and the basal plane of the wurtzite. The preference for nucleation on the (111) surface is evident from the lack of any misoriented nuclei forming on the (11O) step facet as seen in Fig.1. As opposed to a single phase growth on (111) substrates, growth on (100) substrates is composed of multiple phases nucleated heterogeneously at the interface. The presence of the zincblende phase is indicative of more conducive interfacial bonding conditions for the (100) substrate that could be responsible for its stability. However, the wurtzite islands are more numerous than the zincblende islands and therefore could not have been formed by nucleation on inclined (111) facets of the zincblende phase.

It was shown earlier- by Yang *et al*[5] that growth temperature plays a critical role in determining the phase of GaN being deposited on (1 I i) GaAs surfaces. They found that (1i 1) zinc-blende GaN is grown below and (0002) wurtzite GaN above 800°C. However, there was a significant difference in the growth behavior of the GaN on GaAs (11 I)$_A$ surfaces versus (1 1 1)$_B$ surfaces. They found that the crystal linity of the zincblende GaN grown on (i 11)$_B$ surfaces was poorer than on (1 i 1)$_A$ GaAs surfaces. Thus, it could be inferred from their results that it is harder to nucleate the zincblende GaN phase on anion terminated 'R' surfaces. Extending the above assumption to other anion terminated surfaces such as the oxygen terminated (0001) sapphire or (11 1) $MgAl_2O_4$, one could propose that the growth of zincblende GaN would be extremely difficult at any temperature on surfaces terminated by strongly electronegative atoms. Indeed, in this work, although the initial growth temperature (~550°C) was much below 800°C the formation of the zinc-blende GaN phase was suppressed on (1 1 1) $MgAl_2O_4$. on the (100) substrate however, some zinc-blende nuclei have formed during the initial stages of growth with a majority of the nuclei being wurtzite GaN. Therefore, the fourfold (100) substrate surface symmetry does appear to influence the growth of the GaN, perhaps by lowering the activation barrier for the formation of the zincblende phase.

The formation of four wurtzite variants on the (i 00) $MgAl_2O_4$ substrate can be explained by noting the correspondence of the basal planes of each variant with one set of inclined (i 1 1) planes in the substrate. The small angle (~4°C) observed in the (diffraction pattern (Fig. 3) between the basal planes of the wurtzite GaN and the (111) planes of the $MgAl_2O_4$ could be due to the overall slip in the GaN crystal produced by the high density of stacking faults.

Further study is required to understand the relationship between the nature of interfacial bonding and the crystalline phase of GaN stabilized by the $MgAl_2O_4$ surface orientation. A multiplicity of bonds are possible at the interface between the cations, Ga, Al and Mg, and the anions O and N, leading to complex charge balance relationships. Atomic

simulations of the (100) and (111) oriented $MgAl_2O_4$ substrates were performed by Davies ct, al.[6] Although these surface models are highl y idealistic, they serve as a good starting point to understand the interface structure. Acceding to Davies' model the most stable (100) surface is terminated by Mg atoms. in order to maintain charge neutrality on the surface, half of the Mg sites on the surface arc vacant. On the (11 I) surface the most stable surface is initially Al terminated with half the Al sites being occupied. Through a process of 'inversion', some of the Al atoms exchange sites with underlying Mg atoms, giving rise to a more stable surface. Thus the deposited GaN cm these two surfaces sccs very different bonding environments in each case (11 1) and (100) and local variations in bonding on the (100) surface could be responsible for the presence of the five orientation variants.

in summary, wc have examined the growth of GaN by LPMOCVD on (1 1 1) and (100) oriented $MgAl_2O_4$ substrates. The growth on (1 11) substrates results in a single phase wurtzite GaN growth with good crystallinity. Growth on (1 00) oriented substrates results in a multiphase growth with five orientation variants. Interfacial bonding rather than gross lattice mismatch appears to play a kcy role in determining the epitaxial behavior of the GaN films.

Acknowledgments

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List of Figures:

1. High resolution cross-sections] transmission electron micrograph of the interface of the GaN film grown on (1 11) $MgAl_2O_4$. A (1 10) faceted $MgAl_2O_4$ step (see arrow) is seen at the interface.

2. High resolution cross-sectional transmission electron micrograph of the interface of the GaN film grown on (1 00) $MgAl_2O_4$. Three GaN domains are seen: two wurtzite variants and a zinc-blende phase.

3. (loss-sectional diffraction pattern from the GaN film grown on (100) $MgAl_2O_4$.

Fig 1

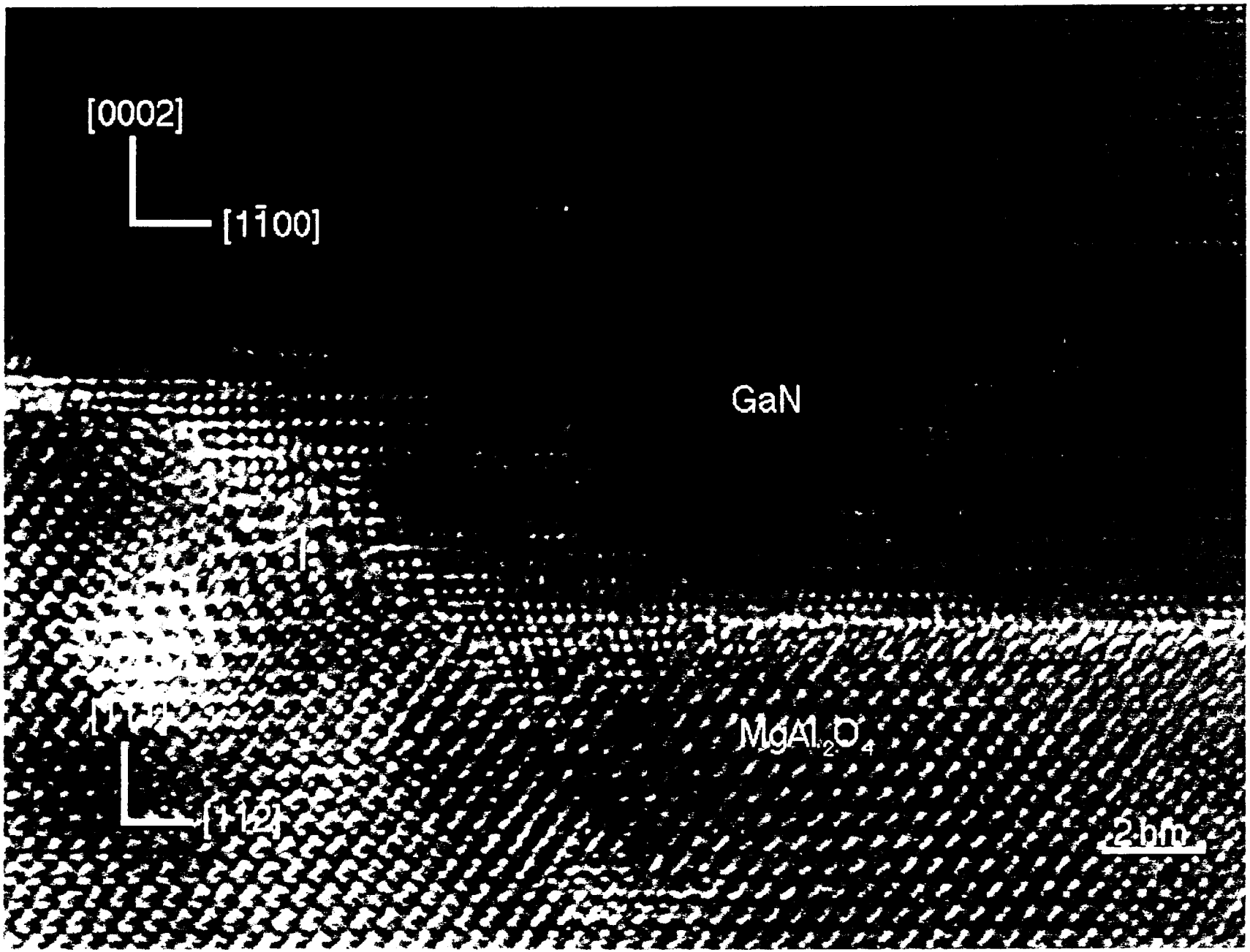
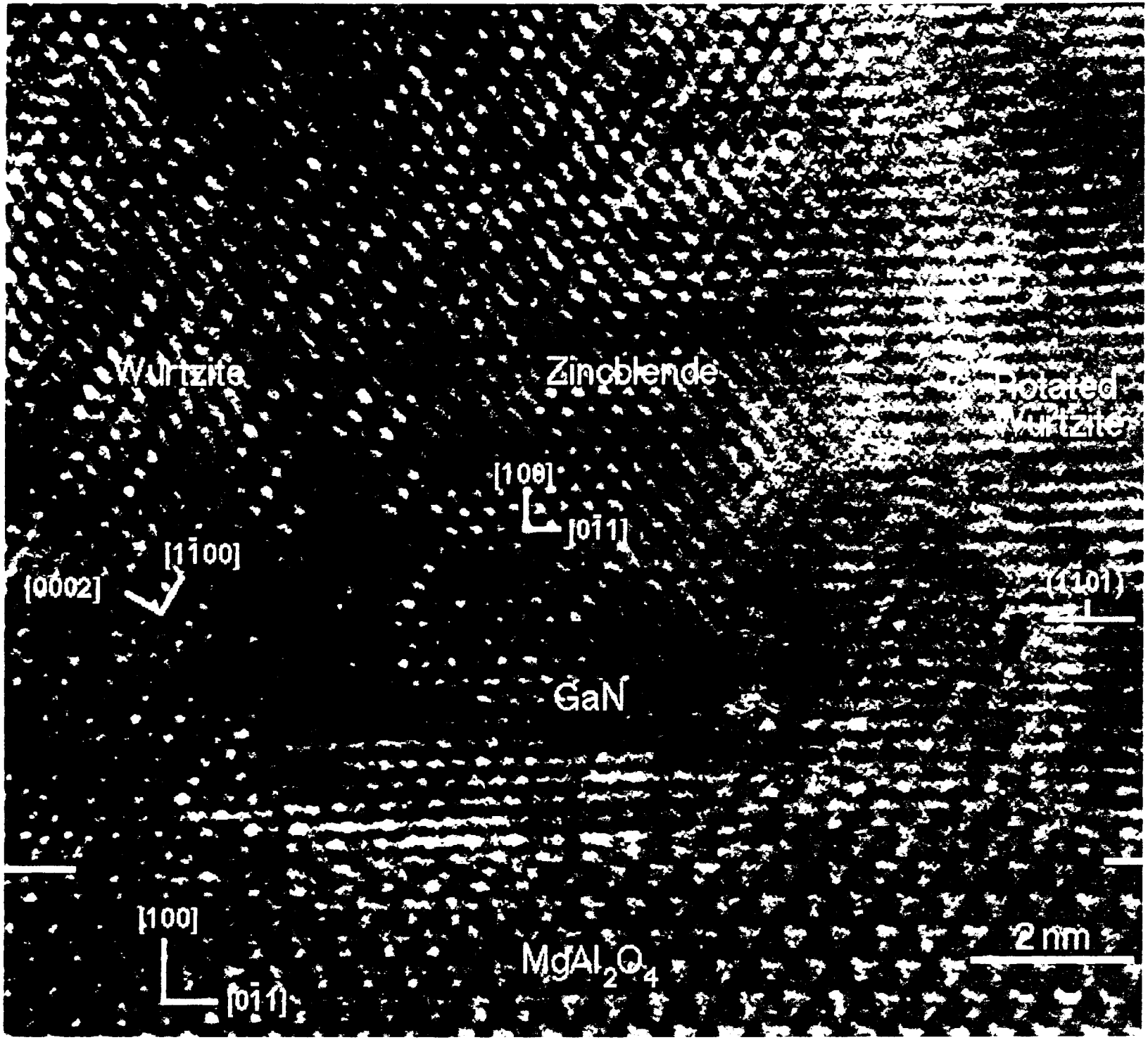
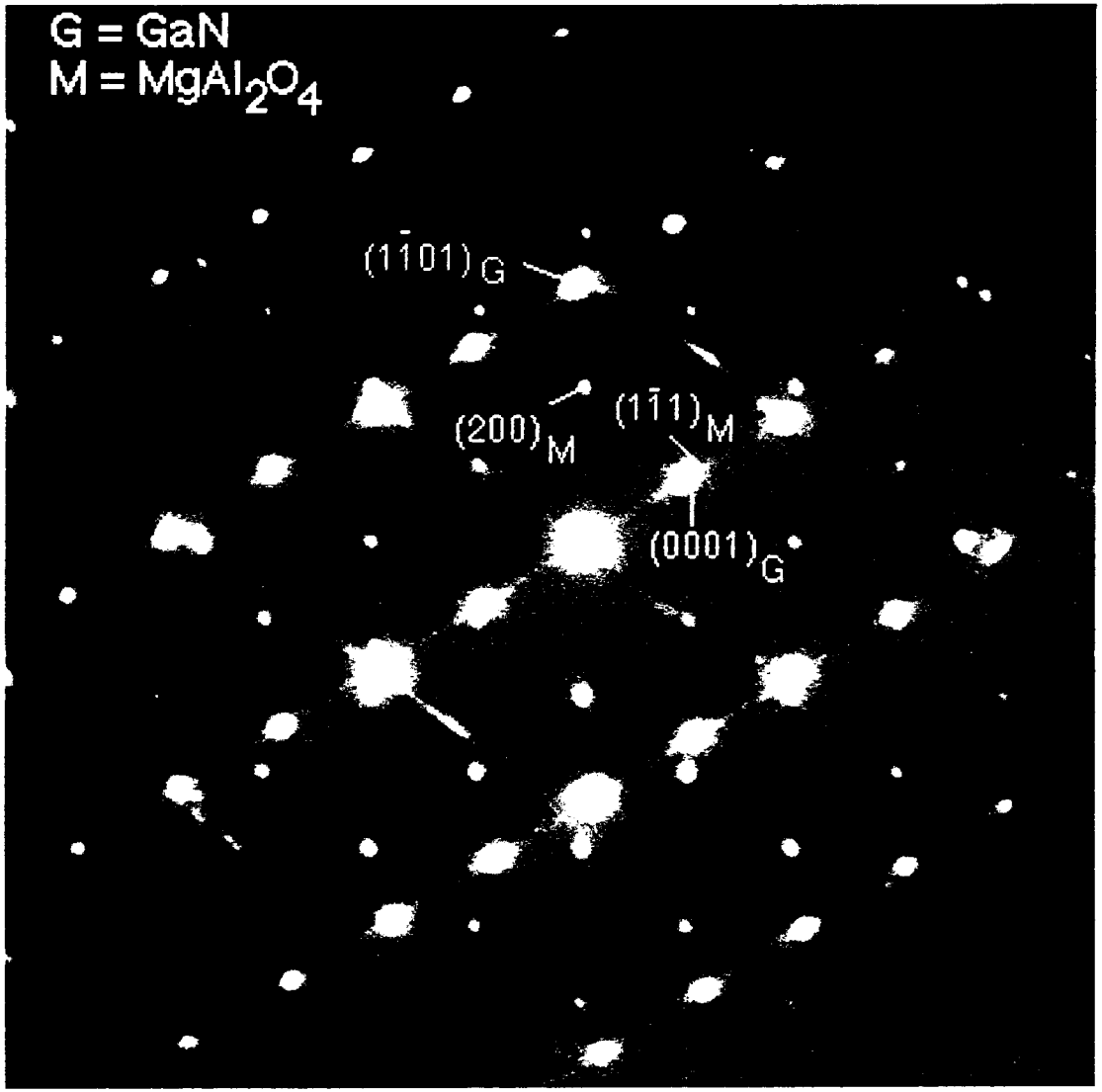


Fig 2


Wurtzite
Zincblende
Rotated Wurtzite
[100]
[01$\bar{1}$]
[1$\bar{1}$00]
[0002]
(1$\bar{1}$01)
GaN
[100]
[01$\bar{1}$]
$MgAl_2O_4$
2 nm


G = GaN
M = $MgAl_2O_4$
$(1\bar{1}01)_G$
$(200)_M$
$(1\bar{1}1)_M$
$(0001)_G$